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## Liquid Crystals

Publication details, including instructions for authors and subscription information:

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**To cite this Article** Bezborodov, V. S. , Min'ko, A. A. , Naumenko, V. I. and Panichev, M. I.(1988) 'Characteristics of relaxational dynamics and the structure of nematogens', *Liquid Crystals*, 3: 6, 901 – 906

**To link to this Article:** DOI: 10.1080/02678298808086547

**URL:** <http://dx.doi.org/10.1080/02678298808086547>

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## Characteristics of relaxational dynamics and the structure of nematogens

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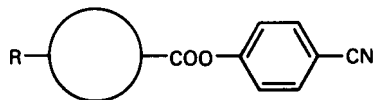
Dielectric relaxation of two esters, 4-cyanophenyl-4-*n*-butyl-(*n*-pentyl)-cyclohex-1-enecarboxylates, in the frequency range 0.5 to 100 MHz, has been investigated for nematic and isotropic phases. Bifurcation of the loss peak for the nematic phase is observed. For the *n*-pentyl compound, we conclude that molecular dimerization could play an essential role in mesophase formation.

### 1. Introduction

It is well known that in liquid crystals consisting of essentially polar molecules dimerization can occur. This causes, in particular, a wide variety of smectic A phase types in certain compounds, re-entrant mesomorphism [1, 2], and other interesting physical phenomena. In this respect, the investigation of the connection between dimerization properties and the molecular packing for the smectic phases seems to be more relevant than for nematics.

A study of dielectric relaxation could contribute, to a considerable extent, to the solution of the problem. We believe that cyano-containing compounds are the most suitable because of their wide diversity; furthermore, their strong polar cyano groups provide large dipole moments which result ultimately, in the dimerization.

When studying the molecular mechanisms of mesophase formation, we consider substances with weak mesomorphic properties, i.e. a narrow temperature range of the mesophase or with a monotropic phase since in this case the limiting, critical characteristics of the molecular structure may be revealed which decide whether the mesophase exists or not. The narrowness of the temperature range is also significant from the experimental point of view because the thermostabilization problems can be minimized. In this respect, cyanophenyl esters of some carboxylic acids with a cyclic fragment



are believed to be the most suitable. Here the constant two-dipole fragment  $-\text{COO}\phi\text{CN}$  is, evidently, the main one that causes dimerization to occur. The rest of the molecule is only a fragment which modifies the properties of the substance as we can see in the table.

The mesomorphic properties of the pentyl and cyclohexyl representatives, as can be seen, are better than those of the butyl and phenyl ones. However, the strong monotropy of the phenyl derivatives produces an obstacle to carrying out the study. More suitable alternatives can be expected if a cyclohexene ring is taken as the cyclic

Literature data on liquid-crystalline cyanophenyl ester transition temperatures.

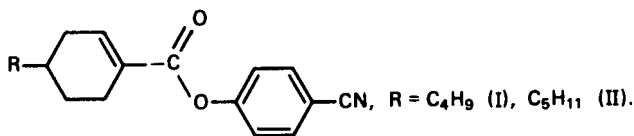
<i>R</i>	Cyclic fragment	Melting point $T_{CH}/^{\circ}C$	Isotropic-nematic temperature $T_{NI}/^{\circ}C$	$\Delta T_{\dagger} = (T_{NI} - T_{CH})/^{\circ}C$	Reference
$C_4H_9$	phenyl	66.1	41.1	-25	[3]
$C_5H_{11}$	phenyl	64.4	55.4	-9	[3]
$C_4H_9$	cyclohexyl	55.8	67.9	+12.1	[4]
$C_5H_{11}$	cyclohexyl	47.2	79.2	+32	[4]

† $\Delta T$  has a negative value for monotropic mesophases.

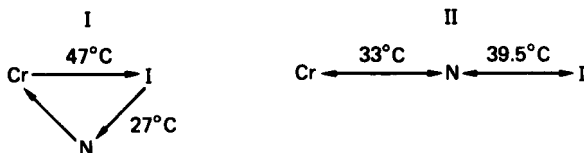
fragment. In such a case the opportunity of rearranging the double bond between positions 1, 2 or 3 would give an additional possibility for the modification. The synthetic methods for preparing similar systems are given in [5, 6].

## 2. Experimental

As a first step we have carried out a study of dielectric relaxation for the cyanophenyl esters of butyl- and pentylcyclo-hex-1-enecarboxylic acids:



These compounds were synthesized in our laboratory. Their purity was verified chromatographically; there were no traces of impurities. Their transition temperatures determined by observation in the measuring cell with a polarizing microscope were



The measurements were carried out with the help of an RF Impedance and Transfer Meter 'Tesla', model BM 538 (ČSSR). The measuring cell was a plane capacitor made of thin glass plates on which sufficiently thick non-transparent nickel electrodes were evaporated. The electrodes occupied only a central part of the glass plates, and because of this geometry there was a possibility of checking visually the phase and the alignment of the sample during microscopic observations.

By treating the inner surfaces of the cell with poly(vinyl alcohol) we succeeded in obtaining homeotropic alignment but not over the whole sample area. So we consider our measurement results only from a qualitative standpoint, being guided by Attard's approach [7] for partially aligned samples. In addition we have not considered it necessary to indicate the extent of the errors on the results shown in the figures. We should only note that the size of the marks of the experimental data is a certain characteristic of the instrumental precision, and the spread of the data can help in visualizing the general accuracy of the experiment.

Check measurements carried out for the empty cell showed that the poly(vinyl alcohol) film did not give any relaxation pattern nor contribute to the results; the

empty cell capacitance was about 40 pF. The sample sizes were about 1 cm<sup>2</sup> by 20  $\mu$ m. The cell provided with the meter probe and a semiconductor temperature gauge was placed in a hermetic aluminium vessel which in turn was immersed in a thermostated water bath. The temperature control had a precision of 0.1°C, the temperature gradient in the cell did not exceed the same value.

The estimates of the dielectric permittivity to be determined were carried out by using parameters of an equivalent scheme, which modelled the measuring process. The elements of the scheme were a spurious capacitance in parallel with the measuring cell and an inductance and resistance in series with the former; the magnitudes of these parameters were defined by the resistance, capacitance and inductance of the inter-connection conductors, the influence of which were especially significant at the high frequency side of the measurement range. The parameter magnitudes were found by calibration with the empty cell, including voltage resonance measurements. It should be noted that the inductance parameters thus obtained lead to clearly incorrect results on the high frequency side of the measurement range. It was possible to correct for this by increasing to some extent the inductance value in the equivalent scheme: the high frequency tails of the Cole-Cole diagrams converged to a single point. However the uncertainty in the parameter values was another reason why we concentrated mainly on the qualitative characteristics of the loss-curve behaviour and, in particular, its temperature dependence.

### 3. Results and discussion

Figure 1 shows the loss curves for the compounds studied at several temperatures. Figure 2 represents the inverse temperature dependences of the logarithm of the relaxation peak frequency (left-hand scale) and the area under the loss curve including portions associated with the wings of the curves which have not been measured

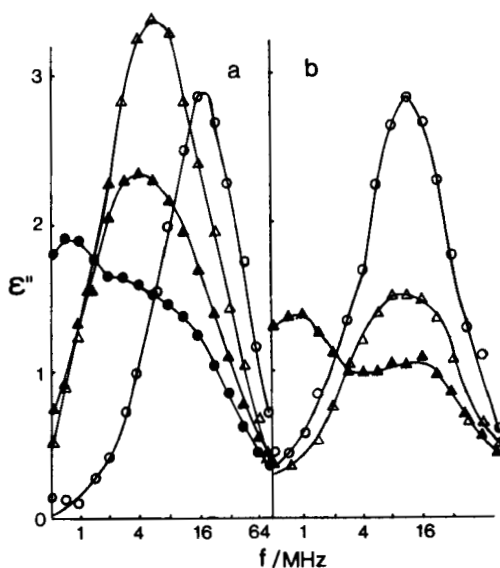


Figure 1. Loss curves [ $\epsilon''(f)$ ] for the cyano-containing nematogens studied. (a) Compound I: ●, 23.8°C; ▲, 26.8°C; △, 31.8°C; ○, 51.1°C, (b) Compound II: ▲, 29.8°C (supercooled nematic phase); △, 40.8°C; ○, 47.1°C.

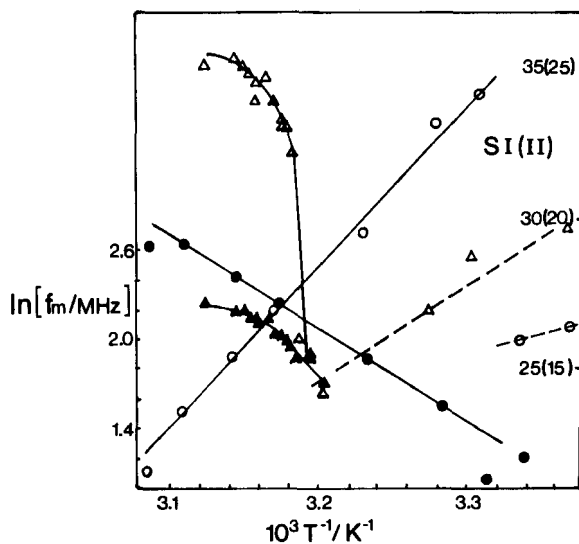


Figure 2. Inverse temperature dependences (circles, compound I; triangles, compound II): (left-hand scale; black marks) of the logarithm of the frequency of the maximum loss in the isotropic phase and (right-hand scale, compound I (compound II, in brackets); open marks) of the area (arbitrary units) under the loss curves.

(right-hand scale). As can be seen from figure 2, the loss curves for the isotropic phase are found almost wholly within the frequency range studied; the unmeasured tails make a negligible contribution and so the approximation methods for them have been of little importance. As to the nematic phase, it is clear that an improper completion of the curves can lead to a very large error for the curve area and so we shall not consider such data when reaching our conclusions.

It can be seen from figure 2 for compound I that the same effective dipole relaxes within the isotropic temperature range since both the logarithm of loss maximum frequency and the integral of the loss curve give linear dependences [7, 8]. The relaxation pattern does not become simpler after the transition to the nematic phase. As we can see from figure 1(a), the loss curve splits into two. The peak frequencies of these do not fit the dependence showing in figure 2 (left-hand scale) and so are not represented in it. Moreover, as can be seen from this figure (right-hand scale) there is a drastic decrease of the loss integral at the transition. In spite of this uncertainty in determining the loss curve area, we can still consider the observed decrease as being related to setting the creation of the well-known antiferroelectric arrangement. More unusual are the very low frequencies of dielectric relaxation in the isotropic phase. Similar low frequency relaxation has already been observed [8] for nematogens with strong lateral dipoles. As can be seen from the data [8], there is no fundamental difference in the relaxation pattern between the isotropic and the nematic phases; all the frequencies of the relaxation maxima fit a single temperature function. The authors of [8] could not find a lower frequency loss peak which could be related to the relaxation of a longitudinal dipole around the short molecular axis, so they concluded that such a process was entirely frozen. However their systems, in contrast to ours, did not possess a strong longitudinal dipole, so this could be a reason for the absence of the loss peak. In our case the expected low frequency relaxation must occur

and could share a part of the observed decrease of the loss curve area. Relaxation at higher frequencies is not likely because the dielectric constant at the high frequency side of the measurement range corresponds approximately to the squared refractive index.

These considerations do not give direct evidence but they do permit us to assume that none of the peaks we have observed is related to  $\tau_{00}$ , the relaxation time of the long-axis molecular dipole moment which in our case is due to the strong dipole of the cyano group rotating around the short axis in a field parallel to the director [7, 9]. According to the same approach, these peaks in the nematic phase will correspond to  $\tau_{01}$  (the relaxation time of the same dipole in a field perpendicular to the director),  $\tau_{10}$  and  $\tau_{11}$  (the relaxation times of the lateral dipole around the long axis of the molecule as well as of the precession of this axis in fields parallel and perpendicular to the director).

One more argument for our assignment can be the absence of a strong retardation of the relaxation process at the nematic–isotropic transition. As we can see from figure 1, the relaxation frequencies observed for isotropic and nematic phases differ only by several orders of magnitude but not hundreds, as we should expect [10].

The more flexible the molecule, the greater is the deviation of the relaxation pattern from a regular semi-circle (see, for example, [11]). Such deviations begin, as can be seen from many experimental results, in the high frequency region of the relaxation pattern: the Cole–Cole diagram corresponding to  $\tau_{00}$  is a semicircle but the high frequency diagrams are significantly oblate. The clear splitting of the loss curve which we have observed for the relaxation as well as the corresponding pronounced splitting of the Cole–Cole diagram provide evidence for a greater deviation of the compound studied from a single component relaxation of rigid dipoles. Of course, the explanation of the splittings as due to the molecular flexibility is not an alternative to the resolution into  $\tau_{01}$ ,  $\tau_{10}$ , etc., but at present we have no criteria for dividing between these mechanisms of relaxation.

All of these considerations are largely related to compound II. There is also a splitting of the loss curve and a comparatively more drastic decrease of the loss integral at the nematic–isotropic transition. However, there are also essential differences; they are shown in figure 2: first, the inverse temperature dependence of the logarithm of the loss peak frequency for the isotropic phase departs from linearity; secondly there is no corresponding linear dependence for the loss integral. Moreover, in the latter case we can see a decrease (not an increase) of this integral when decreasing the temperature within the isotropic phase. This is evidently connected with the effective relaxing dipole being reduced, i.e. there is a certain compensation of the dipole on cooling.

It is known that dimerization processes can be observed in polar liquids of strong dipoles (see, for example, [12]); the energetics of such processes is dependent on the temperature. The accompanying phenomena for liquid crystals are mentioned in §1. In this connection the temperature dependence of the dielectric relaxation we have observed for compound II proves rather definitely that nematic phase formation here is related with dimerization. Then the question arises: would the phase transition be observed at that temperature if there were no dimerization? In other words, might the transition be in the first place as one from monomeric to dimeric liquid? If this were the case the nematic phase would have some unusual features.

We are aware that the assumption about a temperature dependence of the formula of the structural elements (i.e. the change from monomers to dimers) needs additional proof. But this is probably the case.

The reason for the different behaviour of the adjacent homologues can presumably be assigned to a different role of alkyl tails *n*-butyl and *n*-pentyl. Intuitively it is clear that the addition of one methylene-group to a short (three to five carbons) alkyl tail must strongly increase the probability of gauche conformations. It is obvious also that such bend configurations would in general be worse to accommodate the anti-parallel packing usual for rod-like dipoles. We have no detailed data on the packing which occurred in our case but we can assume that an unfavourable antiparallel packing would be more temperature sensitive and would be destroyed on increasing the temperature, thus eliminating a dimeric dipole compensation. This is similar to the behaviour we have observed.

#### 4. Conclusions

- (a) The dielectric relaxation in the MHz region for cyanophenyl esters of *n*-butyl- and *n*-pentylcyclohex-1-enecarboxylic acids is observed both in the nematic and isotropic phases.
- (b) For the nematic phase the loss curve splits, indicating that the relaxation mechanism is complex.
- (c) For the *n*-butyl homologue in the isotropic phase the relaxing effective dipole is constant, as shown by the temperature dependence of the loss maximum frequency and the area under the loss curve.
- (d) At the transition to the nematic phase the area under the loss curve falls drastically for both compounds.
- (e) For the *n*-pentyl homologue, when the temperature of the isotropic phase is decreased the value of the relaxing dipole varies in an extraordinary way: there is a compensation of the dipole probably due to dimerization.
- (f) The difference in behaviour of the two homologues could be attributed to the elongation of the alkyl tail by one methylene group if this would sharply enhance the probability of the formation of bend molecular conformations.

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